Studies on the Oxide Magnets. II : Effects of Bi_20_3 on Strontium and Lead Ferrites

Studies on the Oxide Magnets. II
Effects of Bi_2O_3 on Strontium and Lead Ferrites

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Synopsis

In continuation of the part I, magnetic properties were observed for Sr- and Pb-oxide magnets with or without Bi_2O_3. The mixed powders of Fe_2O_3 from $Fe(CO)_5$, Bi_2O_3 and $SrCO_3$ or PbO were heated at 900°C for 2 hours and sintered at 1000°~1200°C for 15 minutes in the air. The reactions of Pb and Sr ferrites in the range of $Fe_2O_3/SrO < 6$ were completed at lower temperature, and therefore, effects of Bi_2O_3 could hardly be recognized in these systems. The properties of Sr ferrites in the range of $Fe_2O_3/SrO < 6$ were improved by the addition of Bi_2O_3, due to the acceleration in the reaction or in sintering velocity.

I. Introduction

It was stated by the authors in the last report[1] that both $4\pi I_s$ and $4\pi I_r$ of Ba ferrites were increased about 30% and ${}_iH_c$ about 50% by the addition of 1.5~2.5% of Bi_2O_3. Moreover, by reflecting upon the mechanical properties and simple manufacturing process, etc., it was proved that the properties as a permanent magnet were remarkably improved by it. Such an effective element has not yet been found for the oxide magnets, as mentioned in part I, that the effects of Bi_2O_3 on Sr and Pb ferrites were successively studied.

II. Experimental procedure

As the starting meterial, α-Fe_2O_3 was prepared from $Fe(CO)_5$ in order to keep constant the activity for the reaction, and the first grade chemical reagents of Bi_2O_3, $SrCO_3$ and PbO were provided by a certain manufacturer.

After mixing them for 30 minutes in a mechanical mixer, these powders were heated in the air at 900°C for 2 hours, and, after grinding, they were pressed into a cylindrical form with a pressure of 6 ton/cm^2. The specimens were sintered at 1050°~1250°C for 15 minutes in the air. The magnetic properties were observed with an electro-magnet and a ballistic galvanometer.

III. Experimental results

1. SrO-Fe_2O_3-Bi_2O_3 system

The magnetic properties of SrO-Fe_2O_3 system with and without Bi_2O_3 are plotted as a function of the ratio of Fe_2O_3/SrO in Figs. 1~4. That is, Fig. 1 and 3 show

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(1) T. Okamura, H. Kojima, S. Watanabe, Sci. Rep. RITU **A7** (1955), 411.

respectively the $4\pi I_s$ (○ mark) and $4\pi I_r$ (△ mark) of the specimens sintered at 1100° and 1200°C for 15 minutes.

Solid lines in these figures represent the properties of the specimens containing 2.5% Bi_2O_3 and broken line those of 0% Bi_2O_3. Figs. 2 and 4 illustrate ${}_iH_c$ of the specimens, corresponding to the above figures.

$4\pi I_s$ of the specimens without Bi_2O_3 (called *S*-system in the paper) is maximum at the composition of $Fe_2O_3/SrO = 4.7$ (called *P*) and is almost constant in the range $P = 5\sim6$, and then decreases abruptly at $P > 6$, as is shown in Fig. 1. ${}_iH_c$ is almost independent of the value of *P*, but it rises slightly at $P<4.5$ and considerably at $P > 6$. The curve of $4\pi I_r$ is nearly parallel to that of $4\pi I_s$, but it approaches the curve of $4\pi I_s$ in the range $P > 6$, owing to an increase of ${}_iH_c$.

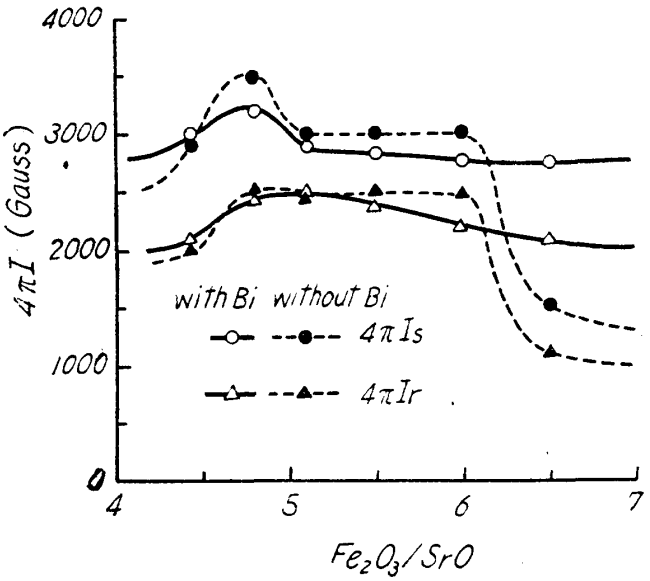

Fig. 1. Saturation and remanent as a function of Fe_2O_3/SrO in the $SrO\text{-}Fe_2O_3$ system sintered at 1100°C for 15 minutes.
Solid line : $Bi_2O_3 = 2.5\%$.
Broken line : $Bi_2O_3 = 0\%$.

As for the specimens with 2.5% Bi_2O_3 (called *M*-system), $4\pi I_s$ is almost equal to that of *S*-system but generally slightly smaller.

However, even in the range $P > 6$ the value doesn't decrease so greatly that it is about two times as large as the value of *S*-system at $P > 6$. ${}_iH_c$ is also nearly equal to that of *S*-system but slightly higher. At $P > 6$, the curve runs almost parallel with the abscissa and it is smaller than ${}_iH_c$ of *S*-system by about 20%, as is shown in Fig. 2.

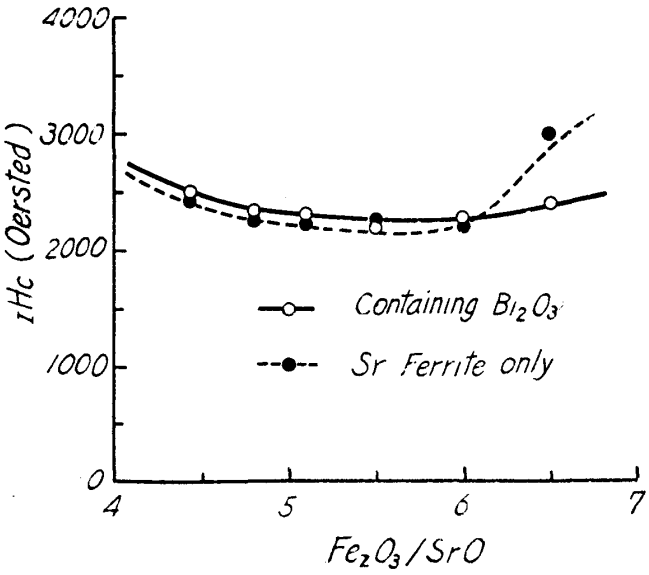

Fig. 2. Coercive force as a function of Fe_2O_3/SrO in the $SrO\text{-}Fe_2O_3$ system sintered at 1100°C for 15 minutes.
Solid line : $Bi_2O_3 = 2.5\%$.
Broken line : $Bi_2O_3 = 0\%$.

The curve of $4\pi I_r$ is parallel to that of $4\pi I_s$ and its height is about 80% of $4\pi I_s$.

Figs. 3 and 4 illustrate the properties of the specimens sintered at 1200°C, and the relation between *M* and *S*-systems is much the same in Figs. 1 and 2, but ${}_iH_c$ of *M*-system decreases abruptly at $P > 6$.

From the above results, effects of Bi_2O_3 could scarcely be observed except in the specimens sintered at lower temperature in the range $P > 6$.

2. SrO-CaO-Fe_2O_3-Bi_2O_3 system

Sr-Ca-ferrites with or without 2% Bi_2O_3 were prepared from Sr-ferrite at the composition $P = 6$, replacing SrO partly with CaO. CaO was added in the form of carbonate, as in the case of SrO, and samples were heated at 900°C. In Figs. 5~8, the magnetic properties of the specimens sintered at 1100° and 1150°C for 15 minutes, are plotted against the contents of CaO.

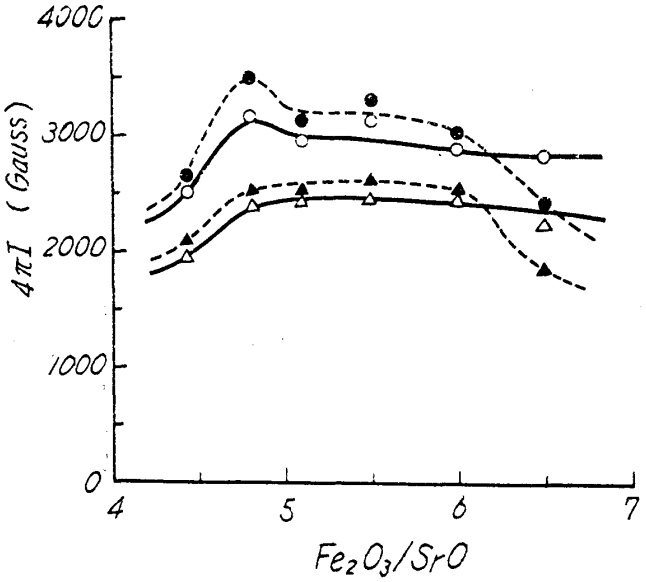

Fig. 3. Saturation and remanent as a function of Fe_2O_3/SrO in the SrO-Fe_2O_3 system sintered at 1200°C for 15 minutes.
Solid line : $Bi_2O_3 = 2.5\%$.
Broken line : $Bi_2O_3 = 0\%$.

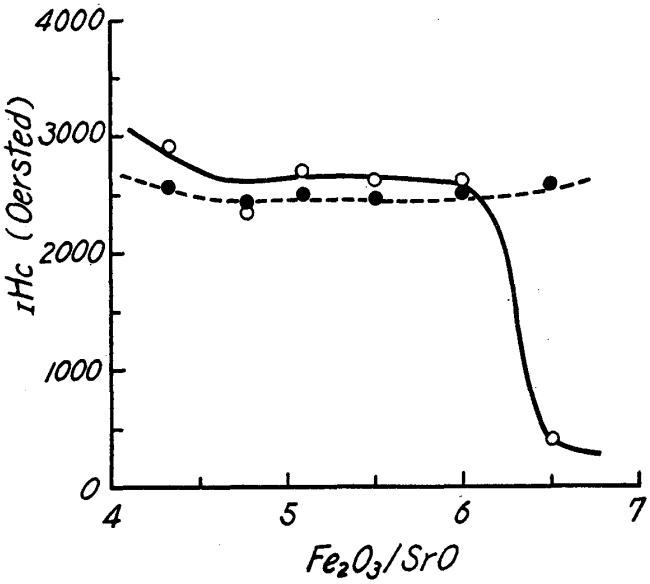

Fig. 4. Coercive force as a function of Fe_2O_3/SrO in the SrO-Fe_2O_3 system sintered at 1200°C for 15 minutes.
Solid line : $Bi_2O_3 = 2.5\%$.
Broken line : $Bi_2O_3 = 0\%$.

The magnetic properties in *S*-system sintered at 1100°C didn't change in the specimens containing less than 3% of CaO as is shown in Figs. 5 and 6. $4\pi I_s$ and $4\pi I_r$ in *M*-system are larger than those in *S*-system by about 80%, regardless of contents of CaO. $_iH_c$ in *M*-system is smaller than that in *S*-system by about 700 oersted but increases with the amount of CaO, and the difference of coecive force in both system becomes only about 200 oersted at 3% CaO.

As for the specimens sintered at 1150°C, $4\pi I_s$ is almost the same as in the case of 1100°C; $_iH_c$ in *M*-system remarkably decreases, and so $4\pi I_r$ in *M*-system is smaller than that of *S*-system by about 500 gauss, as shown in Figs. 7 and 8.

But $_iH_c$ in *M*-system increases with the amount of CaO and, the difference between *M* and *S*-system becomes 800 oersted at 3% CaO. Therefore $4\pi I_r$ in *M*-system increases with the amount of CaO and it becomes about 500 gauss larger than that of *S*-system. That is, $4\pi I_s$ and $4\pi I_r$ are both improved by the addition of Bi_2O_3 and the decrease of $_iH_c$ is comparatively small

in SrO-CaO-Bi_2O_3-Fe_2O_3 system sintered at lower temperature. Effects of Bi_2O_3 are remarkable in this case, but in the specimens sintered at a temperature higher than 1150°C, ${}_iH_c$ decreases so greatly that $4\pi I_r$ becomes smaller than that of *S*-system in spite of a higher value of $4\pi I_s$. However, with 3% CaO added, the addition of Bi_2O_3 brings also better results in these cases.

3. PbO-Fe_2O_3-Bi_2O_3 system

Effects of Bi_2O_3 are scarcely recognized on Pb-ferrite; the observed results of *M* and *S*-system almost coincide with one another in Figs. 9 and 10, in which $4\pi I_s$, $4\pi I_r$ and ${}_iH_c$ are plotted against *P*.

In both systems, $4\pi I_s$ and $4\pi I_r$ are maximum at $P = 4.5$ and decrease monotonously with the increase of *P*. On the contrary, ${}_iH_c$ increases with the value *P*.

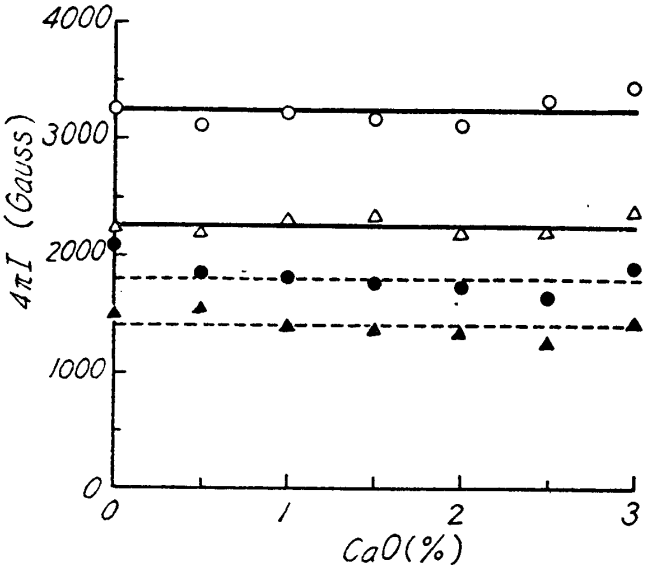

Fig. 5. Saturation and remanent as a function of CaO in the SrO-CaO-Fe_2O_3 system sintered at 1100°C for 15 minutes.
Solid line : Bi_2O_3=2.0%.
Broken line : Bi_2O_3=0%.

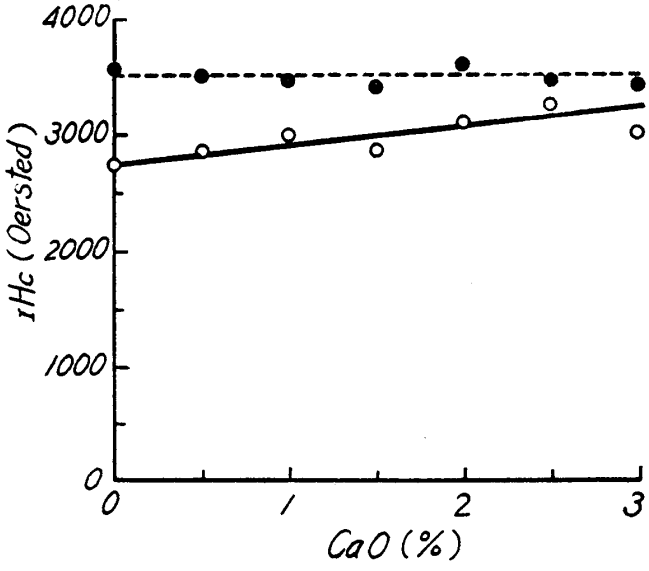

Fig. 6. Coercive force as a function of CaO for the SrO.CaO-Fe_2O_3 system sintered at 1100°C for 15 minutes.
Solid line : Bi_2O_3=2.0%.
Broken line : Bi_2O_3=0%.

IV. Discussion

Differing from Ba-ferrite[1], improvement of magnetic properties in Sr- and Pb-ferrites can hardly be expected by the addition of Bi_2O_3.

Reaction temperatures of these ferrites are lower than that of Ba-ferrite and a heigher value of $4\pi I_s$ is easily obtained under the same sintering condition.

Consequently, the above results may be considered as another proof of the inference made in part I[1], in which Bi_2O_3 might not be regarded as a component of ferromagnetic new phase but merely as an accelerating reagent of the reaction.

The magnetic properties of Ba-ferrite are maximum at the composition $Fe_2O_3/BaO = 5.5 \sim 6$[2][3] and the maximum

(2) C. Okazaki, B. Kubota and S. Mori, Lecture on the Sectional Meeting on Magnetism of Phys. Soc. of Japan at Sendai (July 1953).
(3) H. Hino, ditto.

points cannot be changed by the addition of Bi_2O_3. Therefore the above inference may reasonably be accepted and the results are also not contradictory to the fact that $BaO{\cdot}6Fe_2O_3$ is the ferromagnetic compound in the oxide magnet, as has already been reported[4].

On the contrary, $4\pi I_s$ and $4\pi I_r$ of Sr- and Pb-ferrite are maximum at the composition $P \fallingdotseq 4.5$ and the addition of Bi_2O_3 is effective in Sr-ferrite only in the range $P > 6.5$. The maximum point of magnetic property of Sr-ferrite almost coincides with the results observed by H. Watanabe[5].

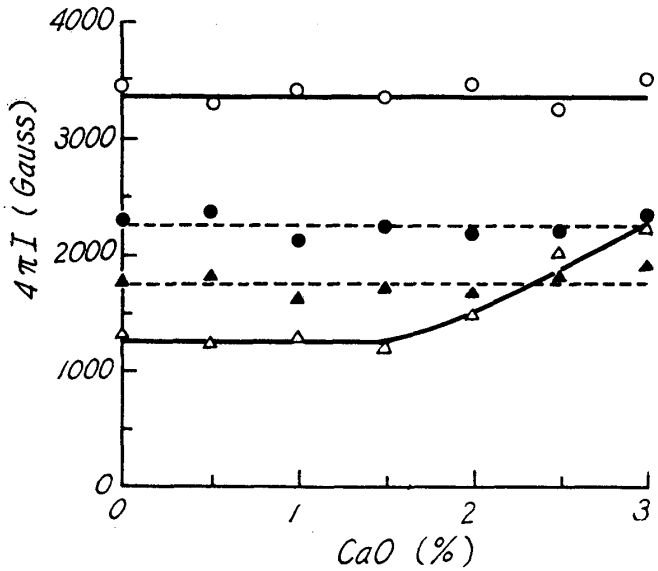

Fig. 7. Saturation and remanent as a function of CaO in the SrO-CaO-Fe_2O_3 system sintered at 1150° for 15 minutes.
Solid line : $Bi_2O_3 = 2.0\%$.
Broken line : $Bi_2O_3 = 0\%$.

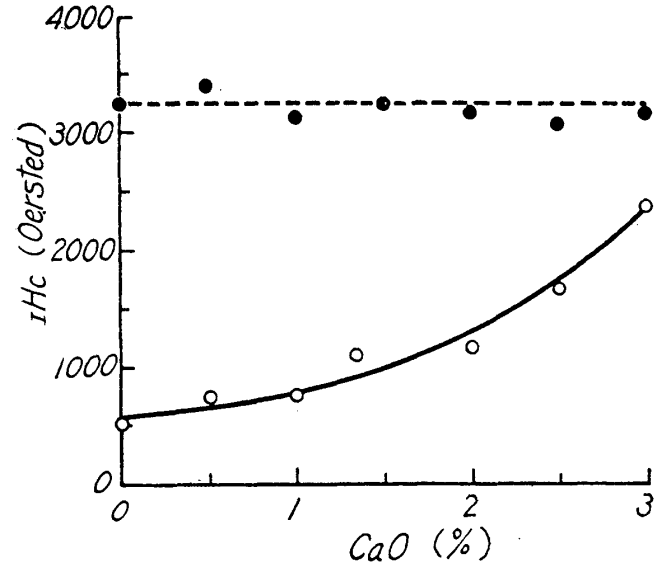

Fig. 8. Coercive force as a function of CaO in the SrO-CaO-Fe_2O_3 system sintered at 1150°C for 15 minutes.
Solid line : $Bi_2O_3 = 2.0\%$.
Broken line : $Bi_2O_3 = 0\%$.

And the following facts may be considered as the cause of the deviation of maximum point from $P = 6$:

(i) The reaction rate at $P \fallingdotseq 4.5$ is especially larger than that of other composition.

(ii) A new ferromagnetic phase $MO{\cdot}4Fe_2O_3$ is formed in SrO-Fe_2O_3 or PbO-Fe_2O_3 system.

(iii) The magnetic properties of the solid solution between $MO{\cdot}6Fe_2O_3$ and $MO{\cdot}Fe_2O_3$ becomes maximum at $P \fallingdotseq 4$.

The data observed by X-ray[5] were contrary to (ii), but further experiments must be performed to make clear the above facts.

Also the explanation as to the effect of Bi_2O_3 on Sr-ferrite at the composition $P > 6.5$, may hardly be given. Because it cannot explain exactly the case like the above phenomenon that the magnetic properties in S-system decreases abruptly at $P > 6.5$.

However, in spite of these

(4) J. J. Went, G. W. Rathenau, E. W. Gorter and G. W. v. Oosterhout, Philips Tech. Rev., **13** (1952), 194.
Japanese Pat. (Notification No. 5734), 1954.
(5) H. Watanabe, J. Japan Inst. Metal. **18** (1954), 588.

experimental results, it seems that the above inference on the effects of Bi_2O_3 may be reasonable yet.

In CaO-SrO-Fe_2O_3 system, Bi_2O_3 also reacts distinctly as an accelerator on the reaction or sintering at a lower reaction temperature.

Summary

In continuation of the part I, magnetic properties were observed in SrO-Fe_2O_3, SrO-CaO-Fe_2O_3 and PbO-Fe_2O_3 systems with or without Bi_2O_3. The results obtained were as follows:

(1) Effects of Bi_2O_3 could not be recognized in Pb-oxide magnets and their magnetic properties were maximum at $Fe_2O_3/PbO \fallingdotseq 4.5$.

(2) $4\pi I_s$, $4\pi I_r$ of Sr-oxide magnets were increased by the addition of Bi_2O_3 only in the range $Fe_2O_3/SrO > 6.0$ but ${}_iH_c$ was decreased. The maximum point of magnetic property was the same composition as Pb-ferrite.

(3) The effects of Bi_2O_3 on SrO-CaO-Fe_2O_3 system sintered at lower temperature were similler to the case of BaO-Fe_2O_3 system but ${}_iH_c$ remarkably decreased in the range CaO $< 1.5\%$ and the diminution was regained at about CaO = 3.0 %.

(4) From the above results, it may be concluded as in the case of Ba-ferrite that the reaction or sintering velocity of these oxide magnets might be accelerated by the addition of Bi_2O_3.

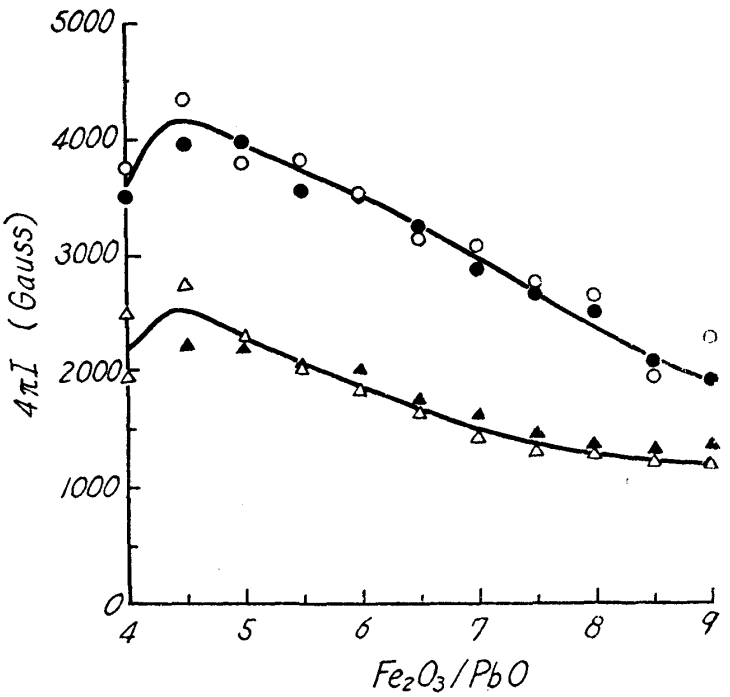

Fig. 9. Saturation and remanent as a function of Fe_2O_3/PbO in the PbO-Fe_2O_3 system sintered at 1150°C for 15 minutes.
○ mark : $Bi_2O_3 = 2.5\%$. • mark : $Bi_2O_3 = 0\%$.

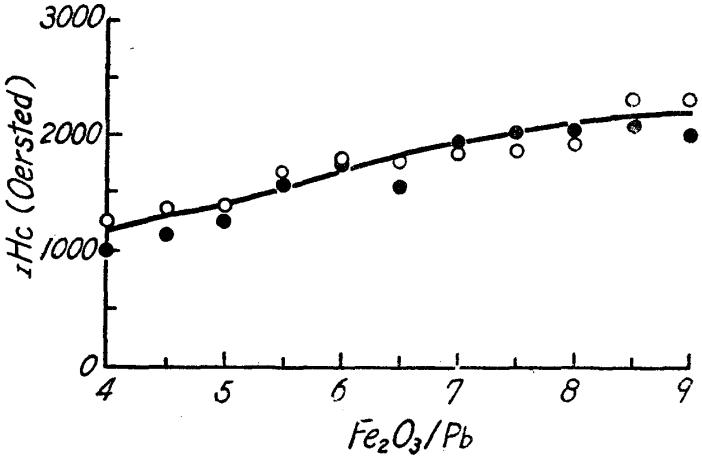

Fig. 10. Coercive force as a function of Fe_2O_3/PbO in the PbO-Fe_2O_3 system sintered at 1150°C for 15 minutes.
○ mark : $Bi_2O_3 = 2.5\%$. • mark : $Bi_2O_3 = 0\%$.

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